Pacific Northwest
NATIONAL LABORATORY

# Low-cost Corrosion Protection for Magnesium

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Project ID # mat150

# Overview

## Timeline

- Start: Jan 2019
- Finish: Sep 2020
- % Complete ~90%

## Budget

- Total project funding
  - DOE: $ 350K
- Funding since inception
  - $ 350K
- Future funds anticipated
  - $ 0

## Technology Gaps/Barriers

- Lack of corrosion resistant magnesium (Mg) alloys
- Lack of cost-effective, durable protective coatings
- Current technology using organic coatings require multiple steps and chemical baths to improve adhesion and porosity-free coatings
  - Environmental concerns

(USDRIVE Materials Technical Team Roadmap, October 2017, Section 5)

## Partners

- University of Oregon
- University of Iowa

# Relevance/Objective

- **Corrosion susceptibility** limits/prevents greater use of Mg alloys in automotive sector despite its light weighting potential
- **Galvanic corrosion** is a major challenge while using Mg alloys in combination with other metals/materials
- **Conventional surface treatment technologies** offer corrosion protection with certain limitations:
  - Chemical conversion: environmental concern, toxic $Cr^{+6}$
  - Anodizing/ Micro-arc Oxidation/ Plasma Electrolytic Oxidation: porous coating, needs sealant
  - Organic coatings: poor adhesion in the absence of pre-treatment, chemical baths are an environmental concern
- *Alternative corrosion protection schemes are needed. PNNL investigating Laser Surface Processing* for improved corrosion resistance in Mg alloys and overcome the challenges of existing coating-based approaches

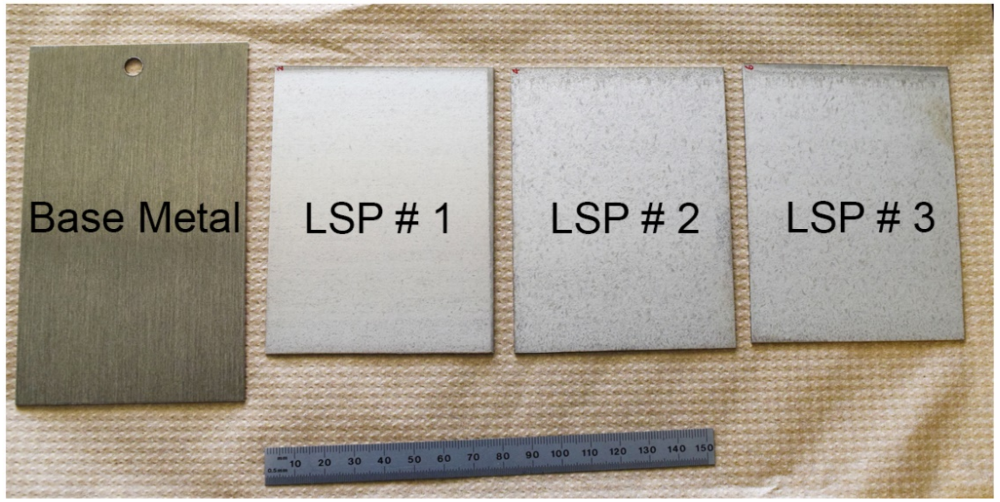
## Project Milestones

| Milestone | Date | Description |
|---|---|---|
| **M1** | 03/31/2019 | Fabricate surface-modified Mg alloy test coupons ✓ |
| **M2** | 06/30/2019 | Perform cross-sectional microstructural characterization of the processed surface to describe elemental and phase distribution ✓ |
| **M3** | 09/30/2019 | Compare mass-loss of un-processed and processed samples tested using ASTM B117 test method ✓ |
| **M4** | 12/30/2019 | Compare mass-loss of surface-modified samples, prepared with various methods, after testing them using ASTM B117 test method ✓ |

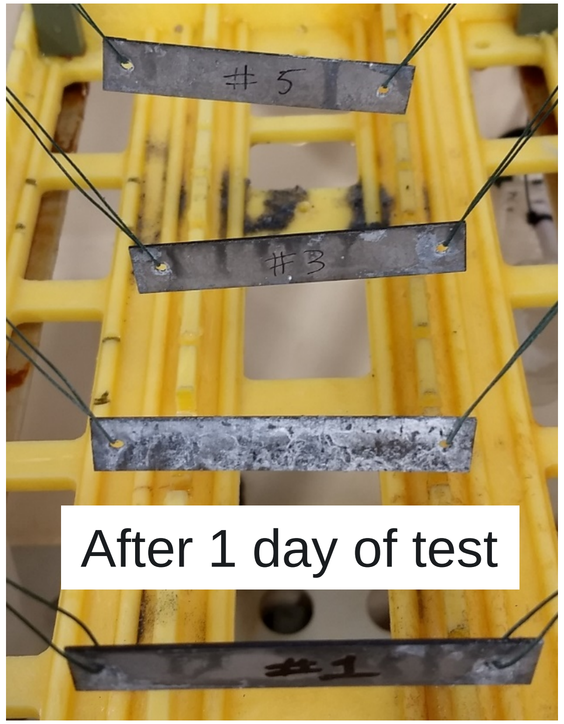
# Approach

- Material: AZ31 Mg sheet
- Surface Modification: Laser-based and non-laser-based processes
  - Laser surface processing @ various pulse energy
  - Hydro-thermal reaction @ various salt composition, temperature
- Corrosion Characterization:
  - ASTM B117 salt fog test for 1500 hours (~ 2 months)
  - Electrochemical tests (OCP (Open Circuit Potential) monitoring, EIS (Electrical Impedance Spectroscopy) scans)
- Microstructural Characterization:
  - SEM (Scanning Electron Microscope)
  - GI-XRD (Glancing Incidence-X-ray Diffraction)
  - XPS (X-ray Photospectroscopy)
  - TEM (Transmission Electron Microscope)
- Develop and Test Hypothesis to identify mechanism(s) behind improved corrosion resistance

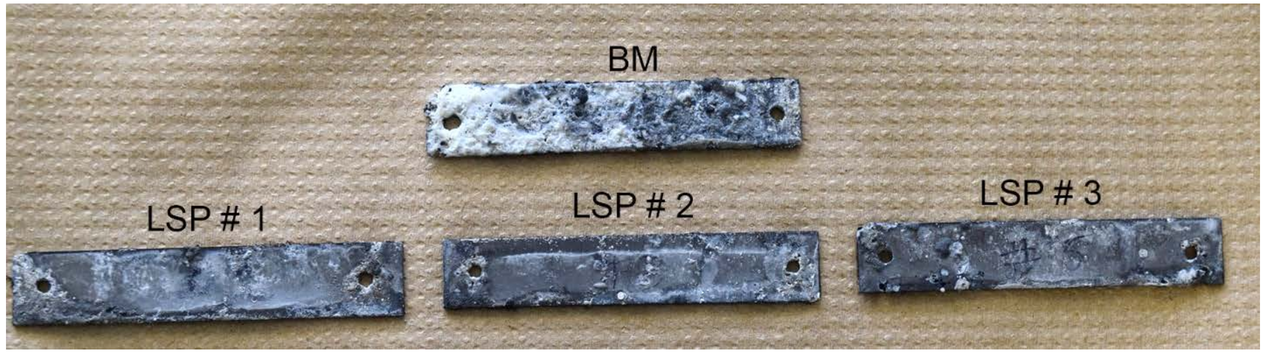
# Technical Accomplishments
## ASTM B117 Test

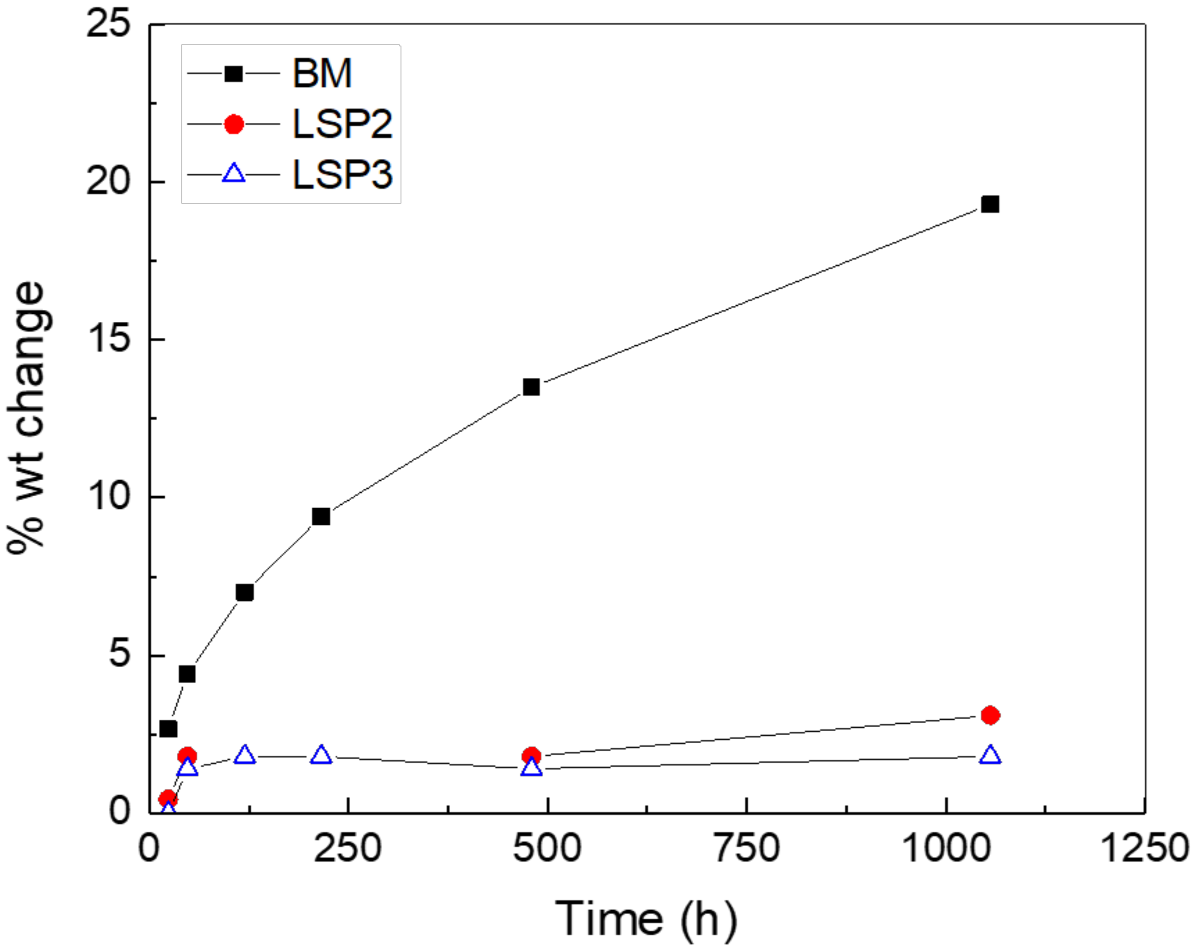



As-fabricated LSP surface



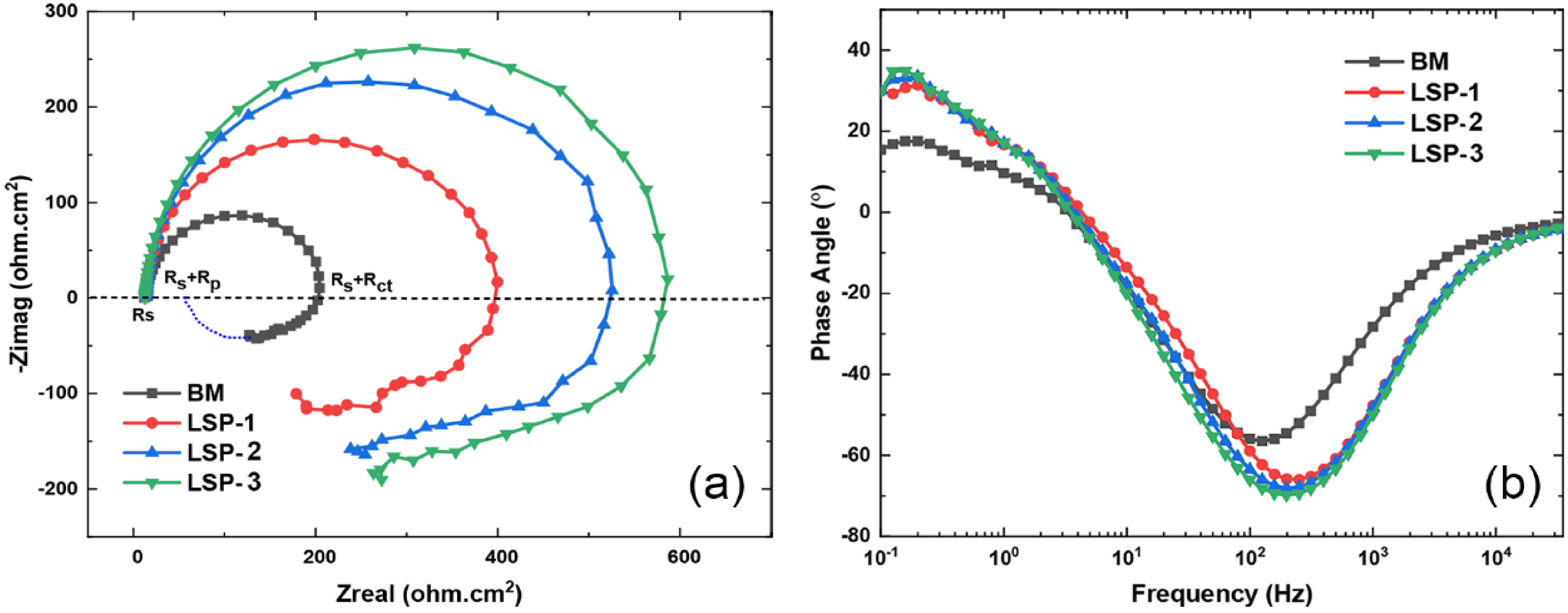

After 56 days of test



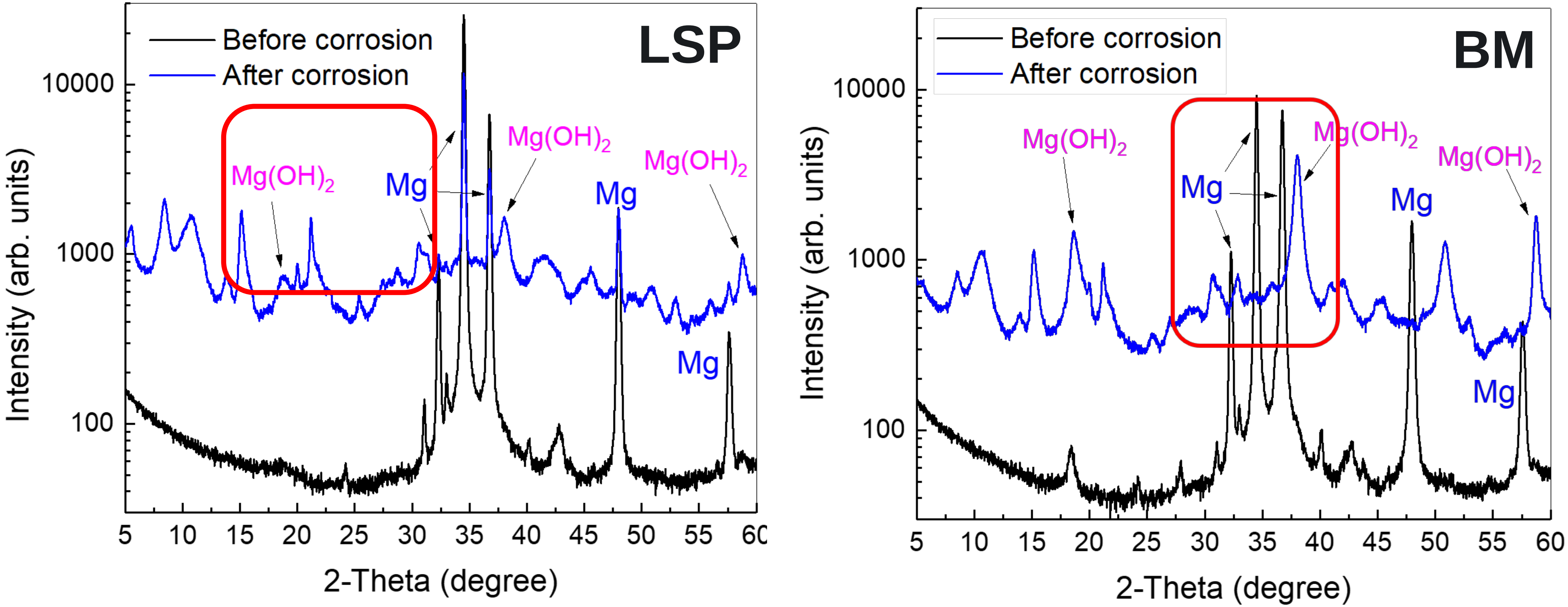

- ASTM B117 test (continuous) for 56 days
- **Lower weight gain in laser surface processed (LSP) samples vs. base metal (BM) confirms improved corrosion resistance imparted by LSP**

# Technical Accomplishments
## Electrochemical Testing (BM & as-fabricated LSP)



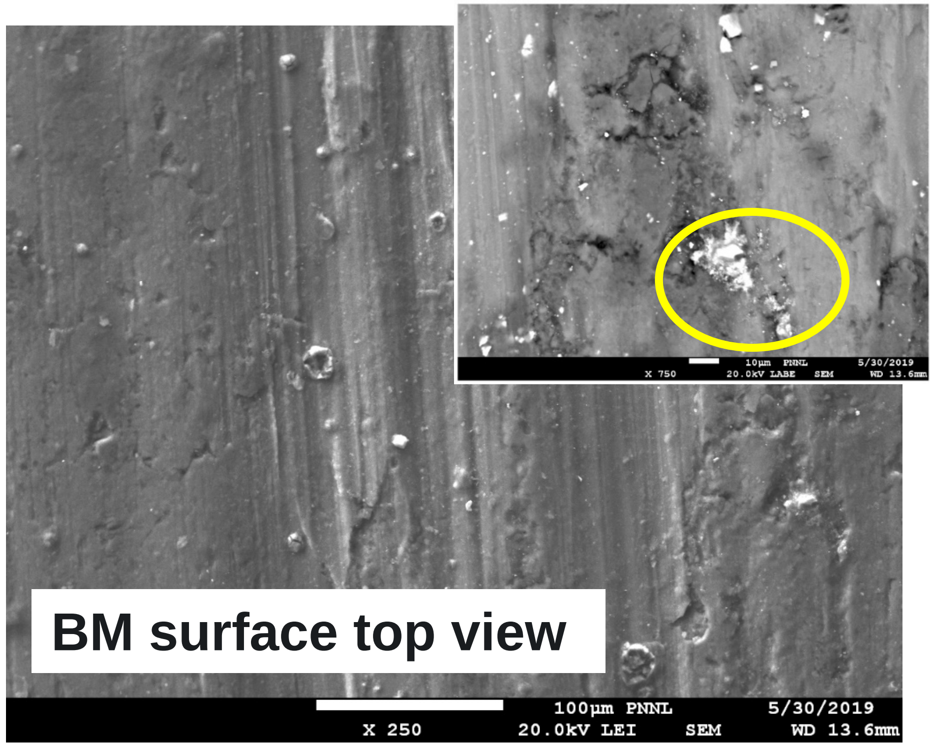

- Electrochemical Impedance Spectroscopy (EIS) scans confirmed improved corrosion resistance in LSP-treated AZ31 samples, since LSP-samples show higher polarization resistance, while Bode plot indicates better capacitive behavior of the surface film in LSP-samples

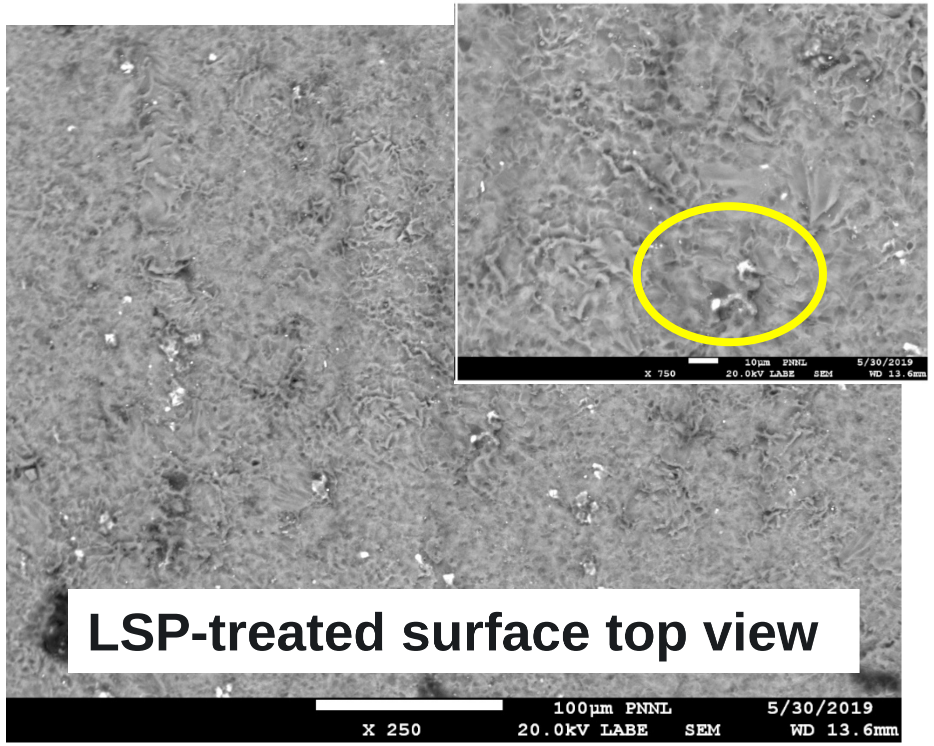
# Technical Accomplishments
## GI-XRD

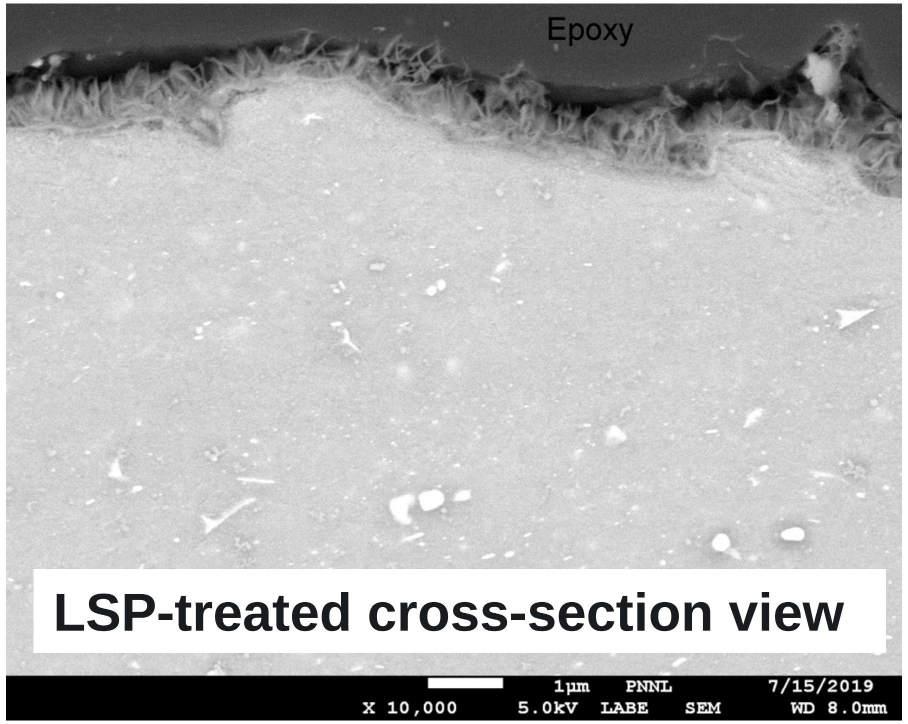



- GI-XRD confirms improved corrosion resistance of LSP-treated AZ31, since XRD peaks corresponding to parent Mg alloy are still visible in LSP-treated samples after the corrosion test

# Technical Accomplishments
## SEM (BM & as-fabricated LSP)

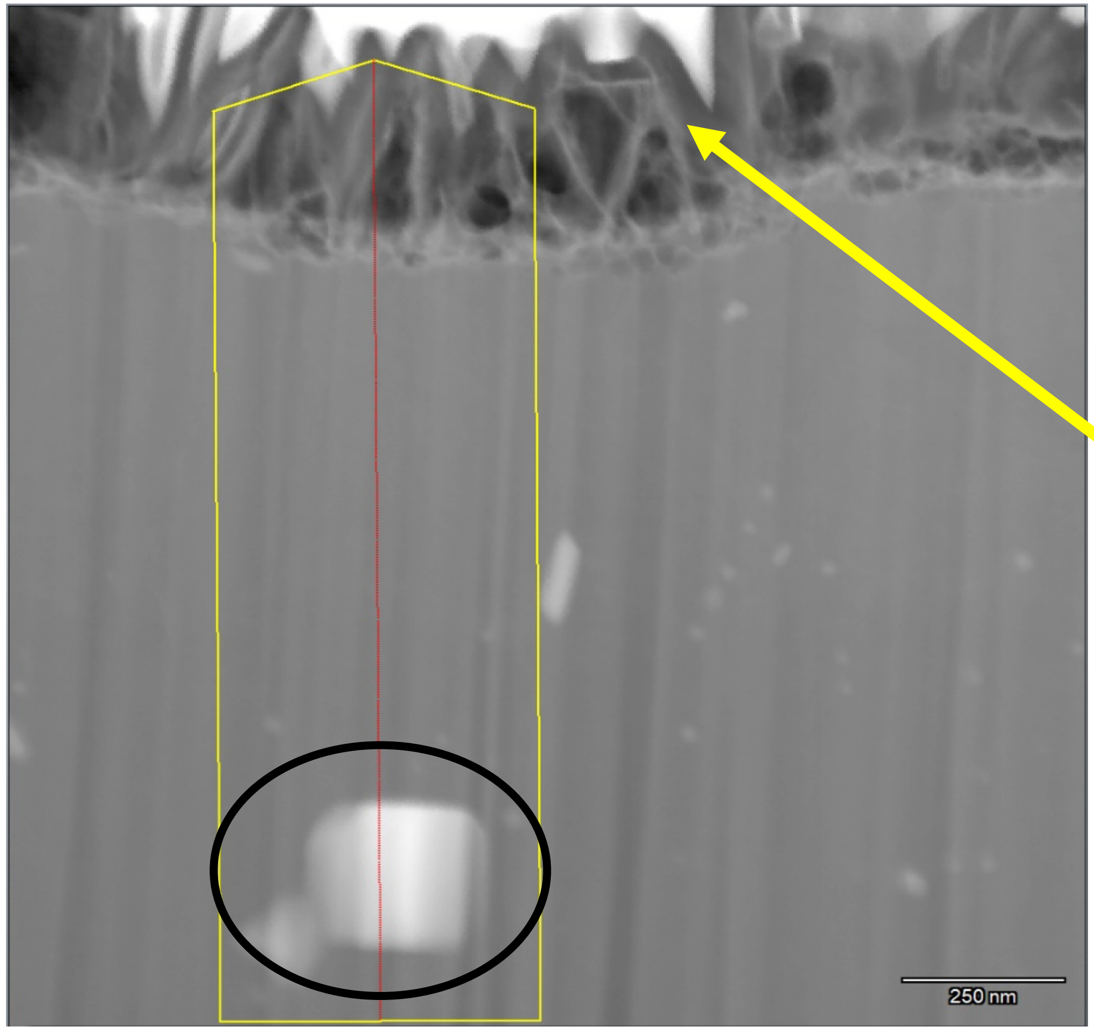


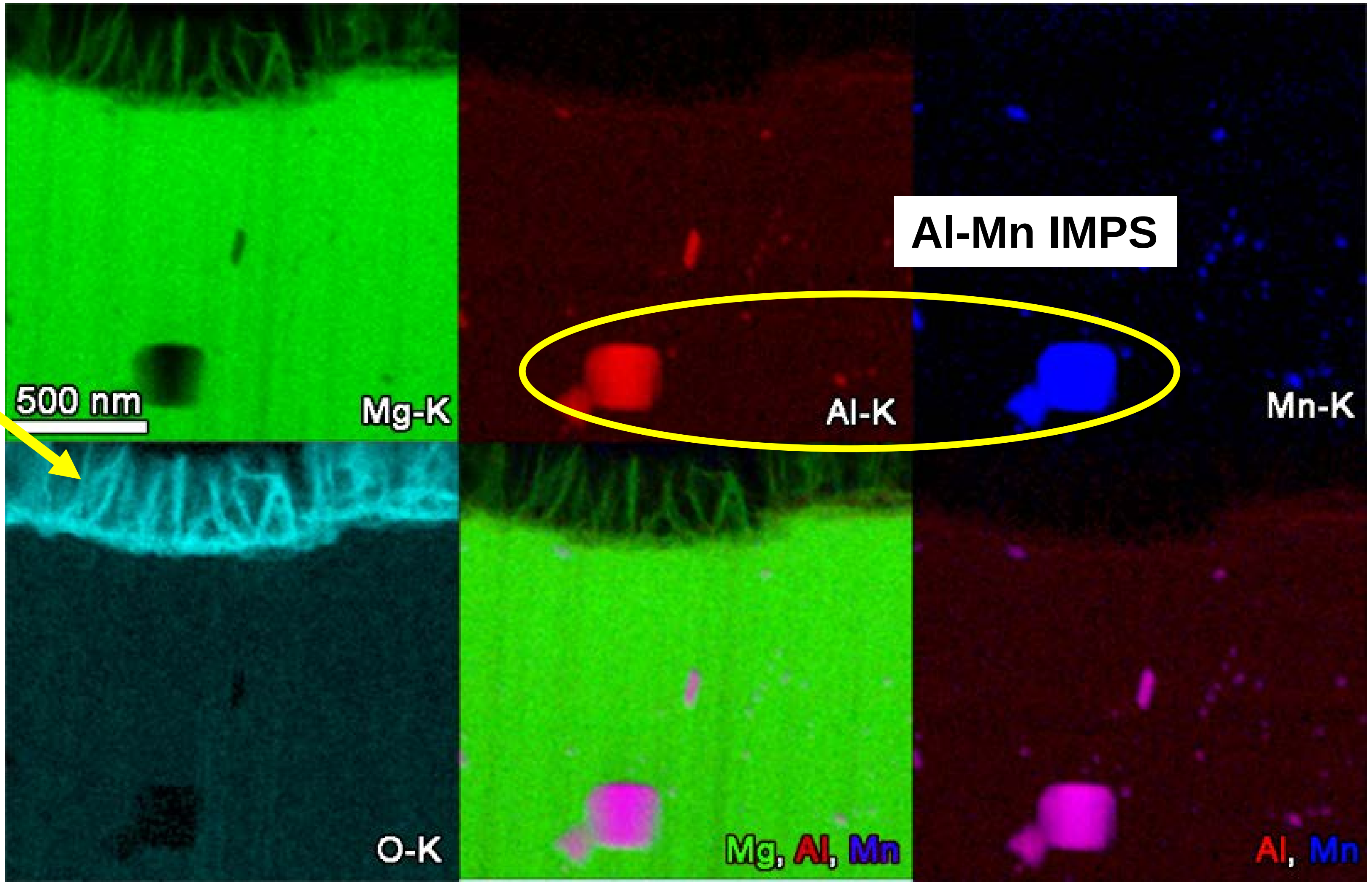




- SEM imaging shows large intermetallic particles (IMPs) on the surface of AZ31 BM
- **LSP treatment results in significant refinement of IMPs**
- **LSP-treated samples show formation of ~0.5 µm thick film on the surface**

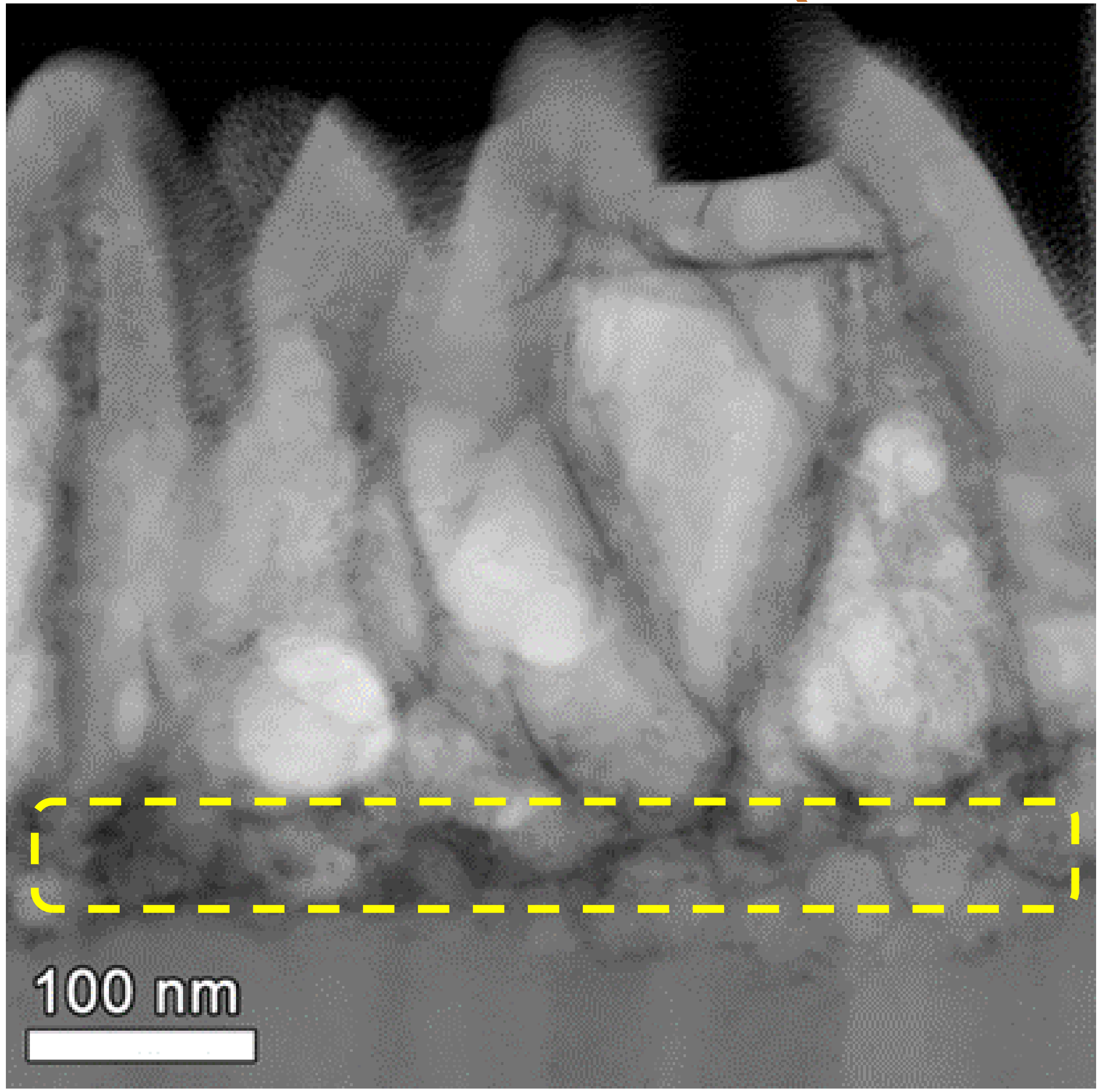
# Technical Accomplishments
## TEM & EDS (LSP, as-fabricated)

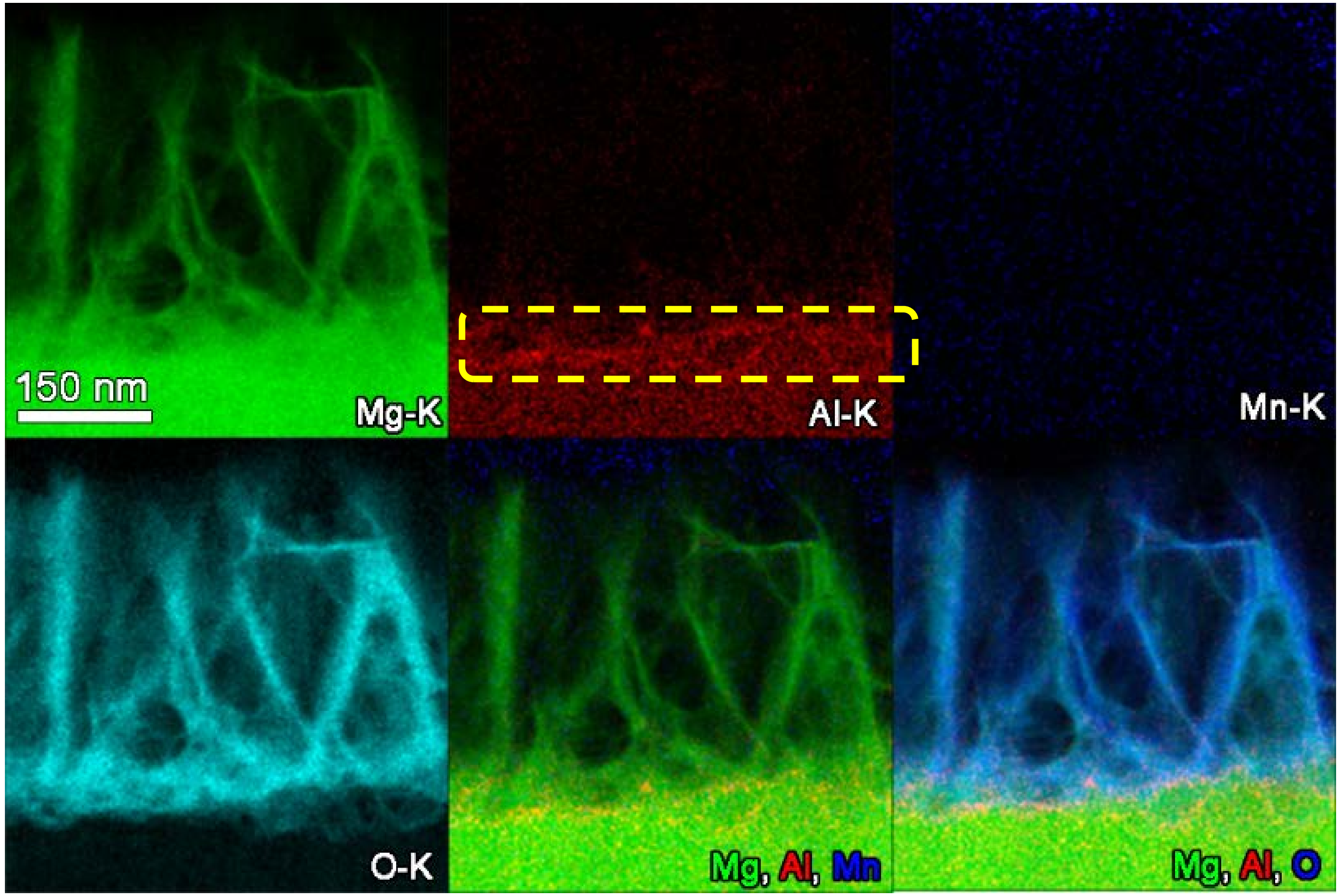



- **TEM analysis confirms ~0.5 µm film formation on LSP-treated surface**
- **EDS elemental mapping indicates the surface film to be oxygen-rich**

# Technical Accomplishments
## TEM & EDS (as-fabricated LSP)



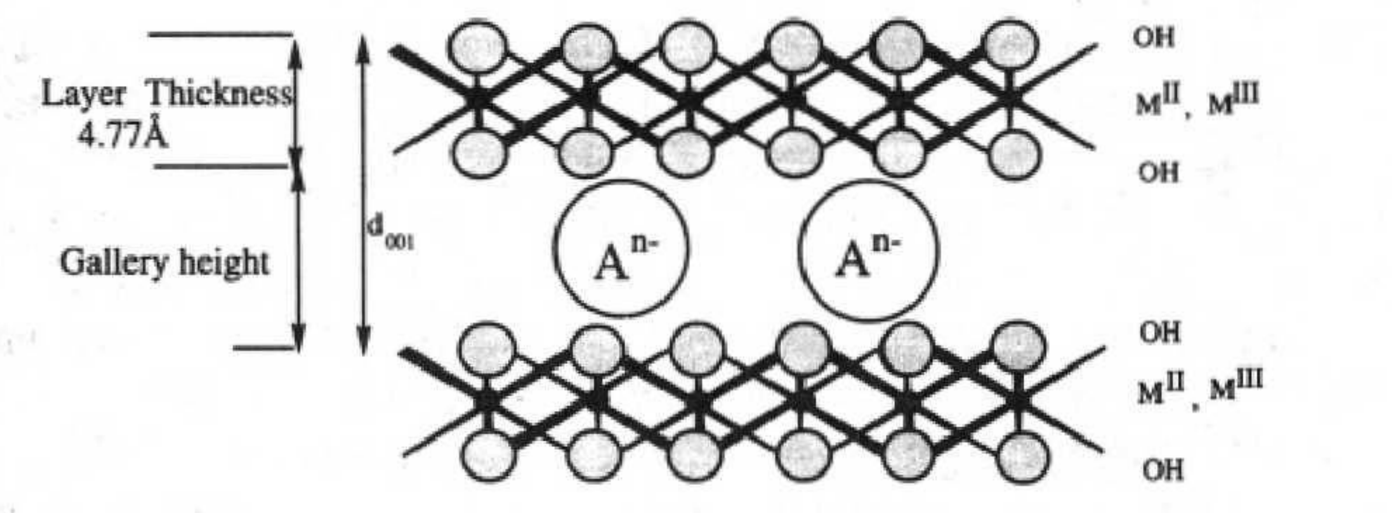

- **EDS elemental mapping detects Al-enrichment at the base of the top surface film on LSP-treated side**

# Technical Accomplishments

## Summary of LSP-induced Microstructure

- ~0.5 μm oxygen-rich surface film on LSP side
- Size reduction of Al-Mn IMPs in the first ~1 μm underneath the LSP side
- Slight Al-enrichment at the surface film/AZ31 matrix interface
- Brucite [$Mg(OH)_2$] is the major corrosion product in untreated BM. Possible modification of brucite-like structure can happen through the formation of **layered double hydroxide (LDH) phase in LSP-treated AZ31**

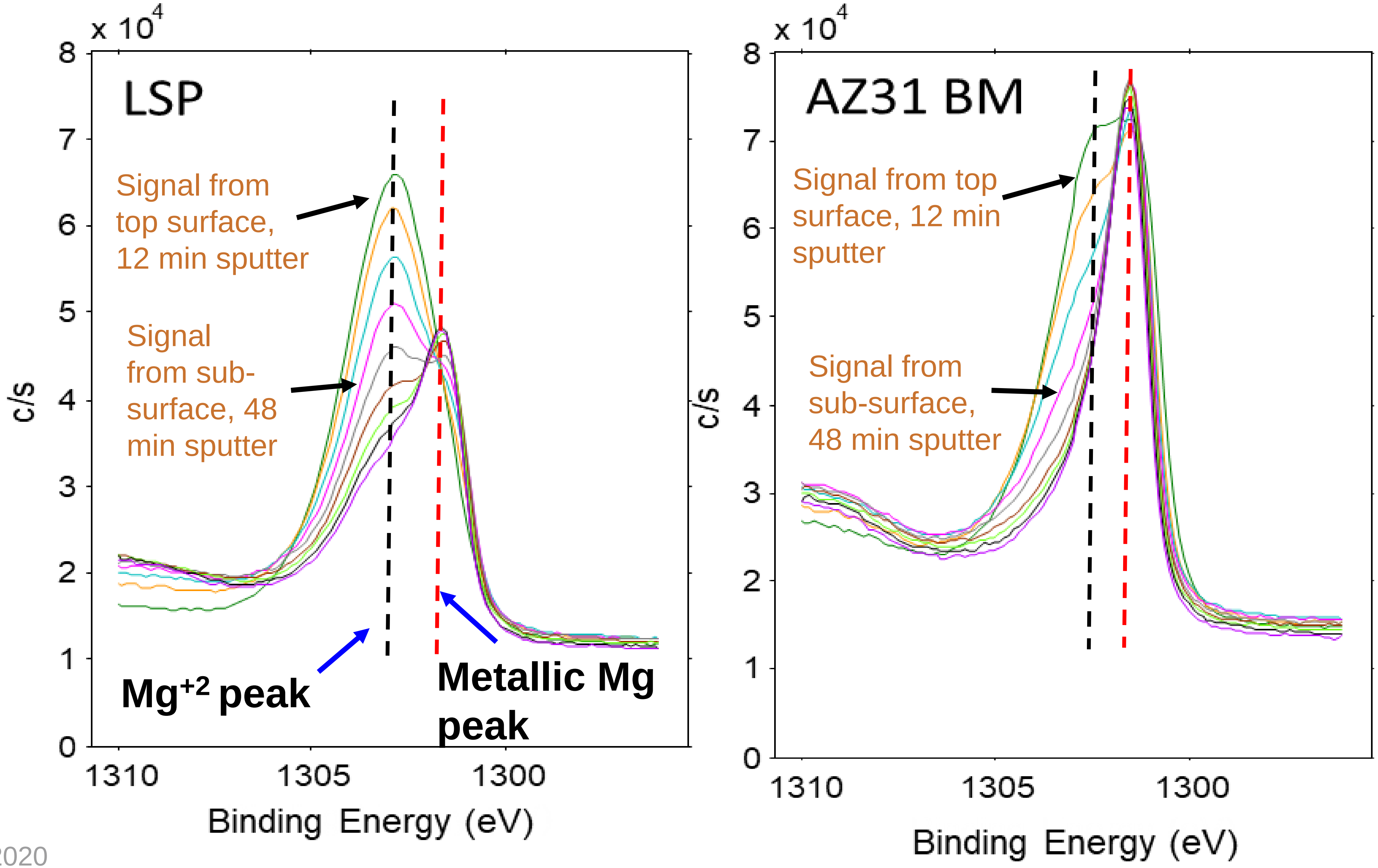
***Presence of LDH-like structure on LSP-treated side should be associated with the presence of $Al^{3+}$ type cations, which replaces some of the $Mg^{2+}$ cations in the top surface film***




*Inorg. Chem.* 1995, 34, 4, 883-892

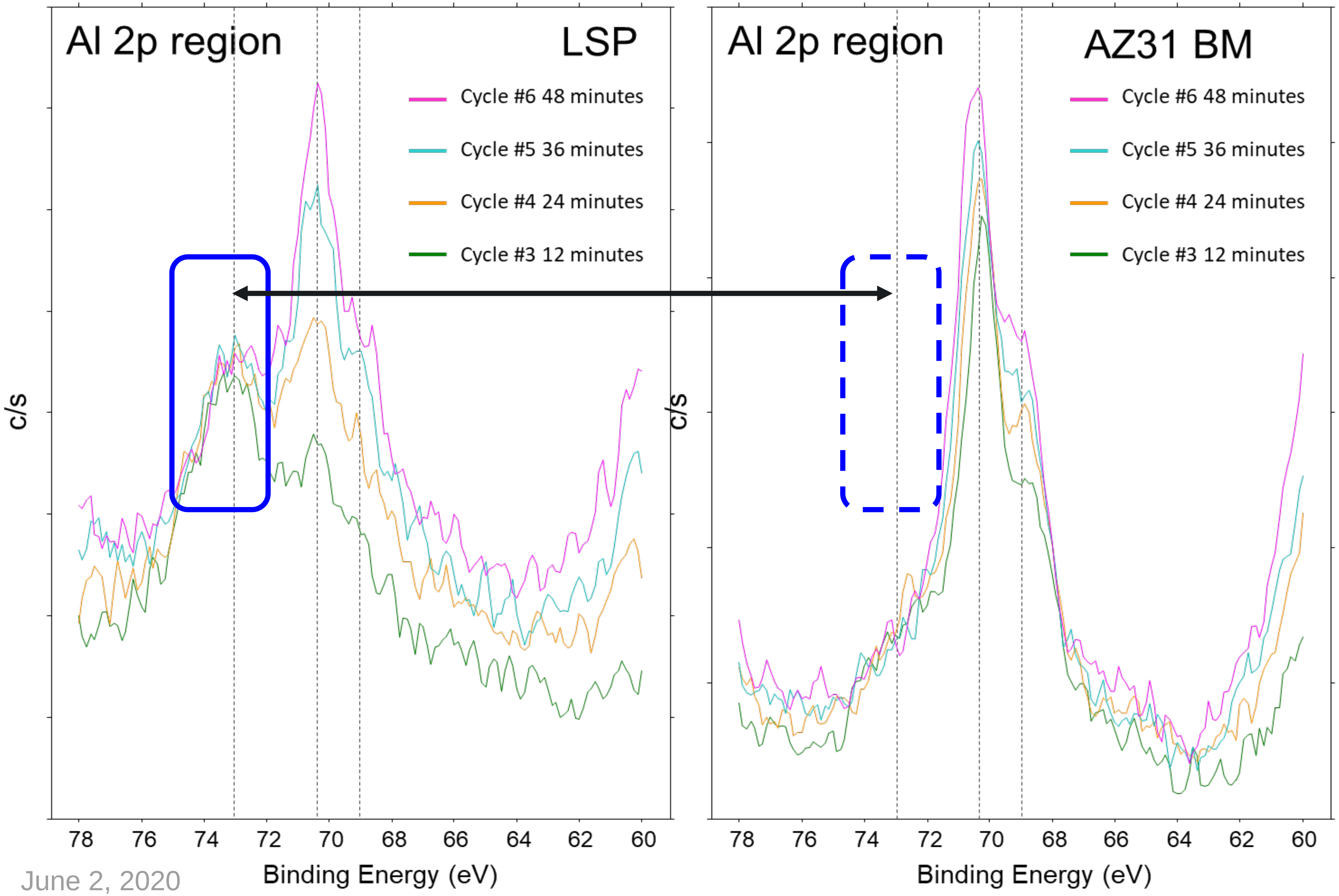
# Technical Accomplishments

## XPS (BM & as-fabricated LSP)



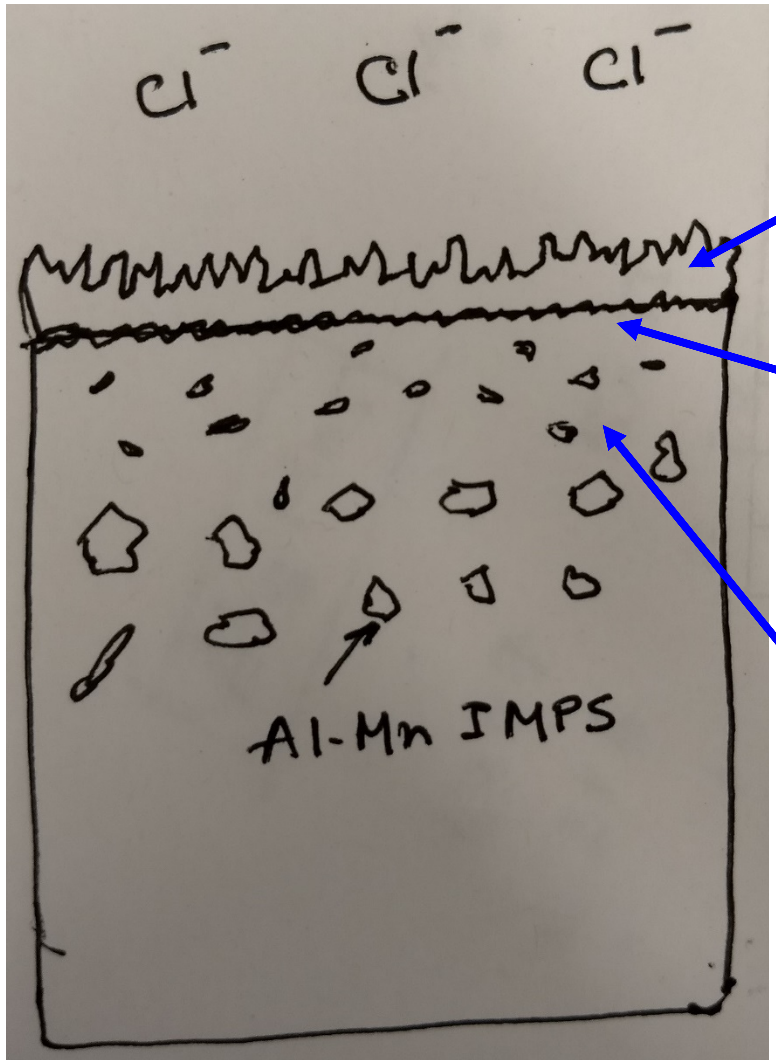

- **XPS shows presence of $Mg^{+2}$ peak in LSP sample surface film**

# Technical Accomplishments
## XPS (BM & as-fabricated LSP)




- XPS confirms presence of Al ion, ~ 73 eV in the surface film of LSP sample → **Formation of mixed (Mg, Al)-oxide/hydroxide after LSP**
- **Clear absence of Al ion in BM top surface**

# Technical Accomplishments
## Hypothesis for LSP-induced Corrosion Resistance



Schematic cross-section of laser processed AZ31 alloy

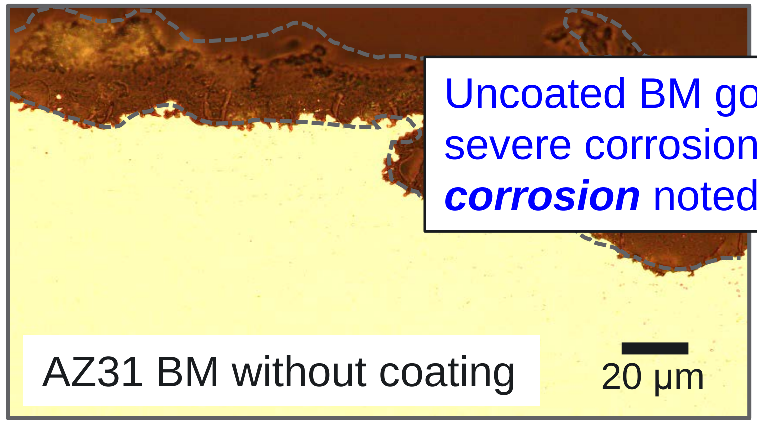
- ~ 0.5 µm thick surface film with finger like morphology, possibly MgO type phase, with additional Al-enrichment (XPS)
- 20-30 nm thick subsurface film, Al-rich, suggested by TEM-EDS
- Possible size reduction of Al-Mn IMPS within the first 1-2 µm from top on the LSP side

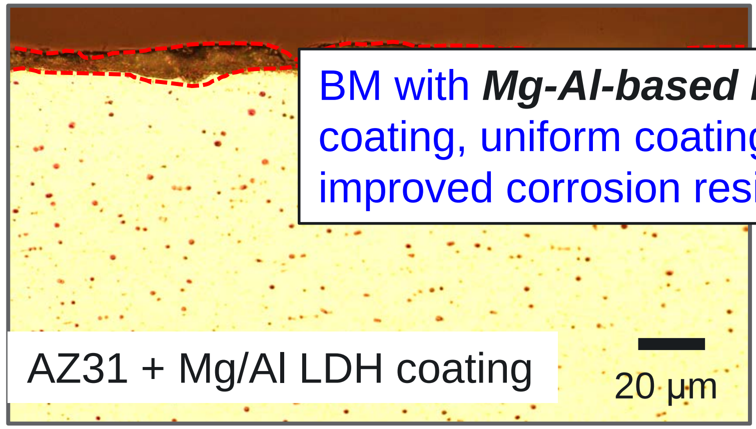
**Anodizing**, i.e., insulating ceramic oxide/hydroxide layer on the surface

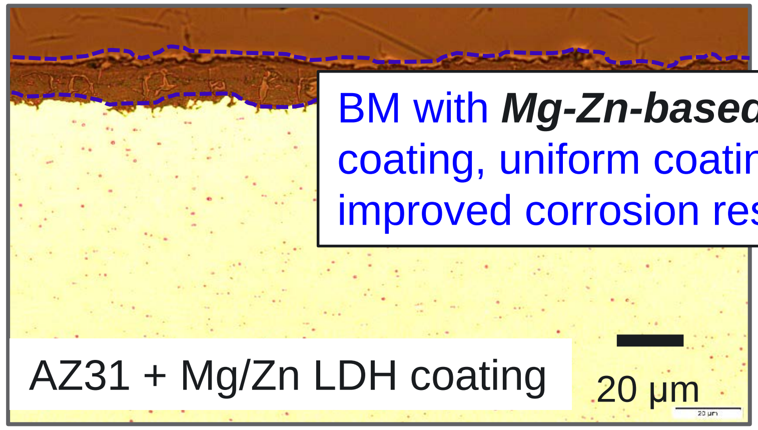
Al-Mn IMPs act as cathodic sites to anodic Mg. **Lower cathode to anode ratio** → Reduced micro-galvanic coupling

**Major difference between LSP and BM is the presence of Al ion in the top surface film after LSP treatment**

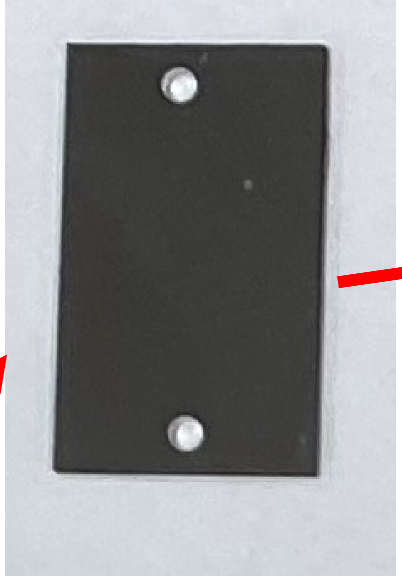
# Technical Accomplishments
## Hydrothermal reaction for LDH coatings




At start



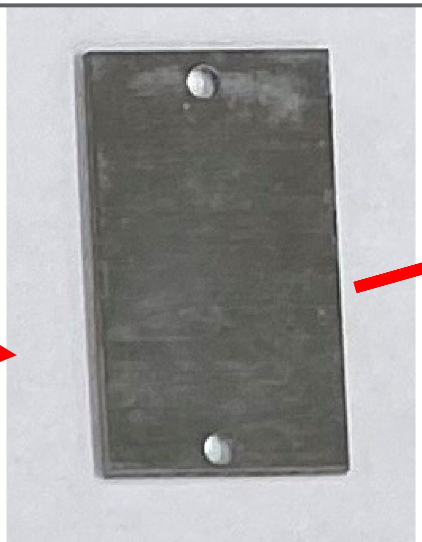
After 312 h

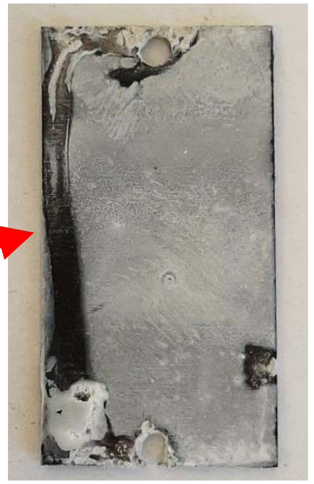
After 1008 h

**% wt. gain ~ 0**

AZ31 BM, 312 h

**ASTM B117 test up to 6 wks (1008 h)**





**% wt. gain ~ 0.5**

AZ31 BM, 1008 h

**% wt. gain ~ 2.0**

**LDH-type coatings prevent localized pitting → Improved corrosion resistance**

# Response to Reviewer's Comments

- *".. it is difficult to anticipate whether the team will successfully elucidate the mechanisms.."*
  - ***Using various analytical characterization tools, we have been able to come up with a possible hypothesis behind improved corrosion resistance observed in LSP-treated AZ31 alloy***
- *"..While the presentation notes improved atmospheric corrosion resistance in surface-modified AZ31B sheet, this does not necessarily mean the surface-modified material will exhibit improved corrosion resistance in aqueous environments (especially with salt).."*
  - ***ASTM B117 test, and, subsequent other electrochemical tests confirm the effectiveness of laser surface processing in improving the corrosion resistance of AZ31 alloy***

# Collaboration and Coordination

- University of Oregon
  - Electrochemical testing
- University of Iowa
  - Surface process development

# Proposed Future Work

- Identify corrosion mitigation mechanism(s) in Mg-Zn LDH coatings:
  - Advanced electrochemical testing to correlate microstructure with corrosion behavior
  - In-situ analysis (corrosion imaging in TEM)
  - Effect of second phase particles; Mg-alloy family (AM, AZ, ZEK)

- Work with industry partners:
  - Continuous process for LDH coating
  - LSP to protect laser-welded dissimilar joints

*Any proposed future work is subject to change based on funding levels*

# Summary

- Laser surface processing (LSP) can markedly enhance corrosion resistance of AZ31 alloy
    - It appears that the laser treatment leads to easier formation of Mg/Al-layered double oxide (LDH) film during corrosion test.
    - LDH film, a possible modification of $Mg(OH)_2$, provides better corrosion resistance through a uniform film formation, and resisting localized pitting corrosion
    - LSP-induced size reduction of Al-Mn intermetallics in subsurface layer (first 1-2 μm) may contribute to enhanced corrosion resistance by lowering cathode to anode area ratio
- Mg-Zn LDH coatings are promising candidates → Prevent localized pitting corrosion in AZ31

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# Thank you

# BACKUP SLIDES

# Low-cost Corrosion Protection for Magnesium

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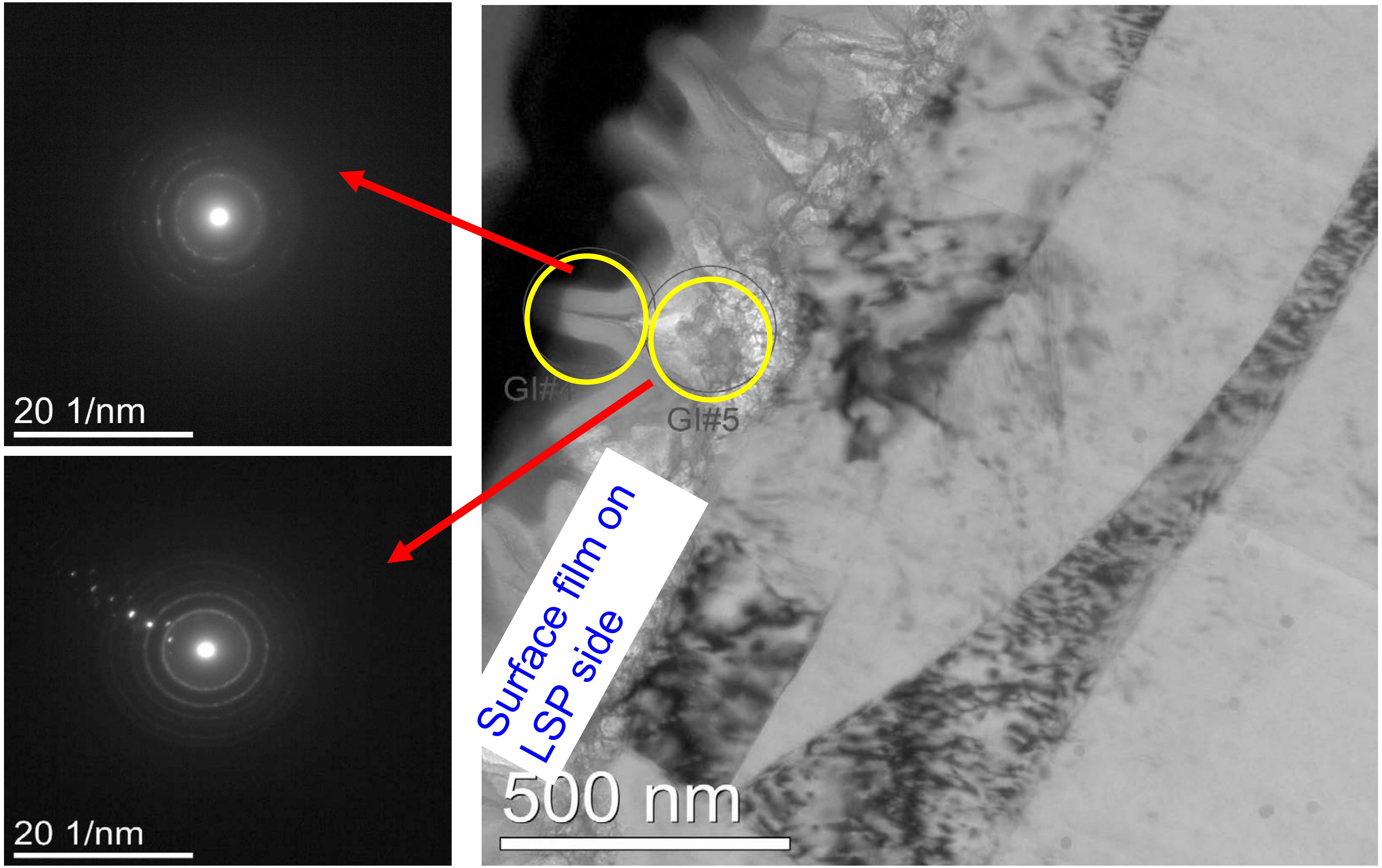
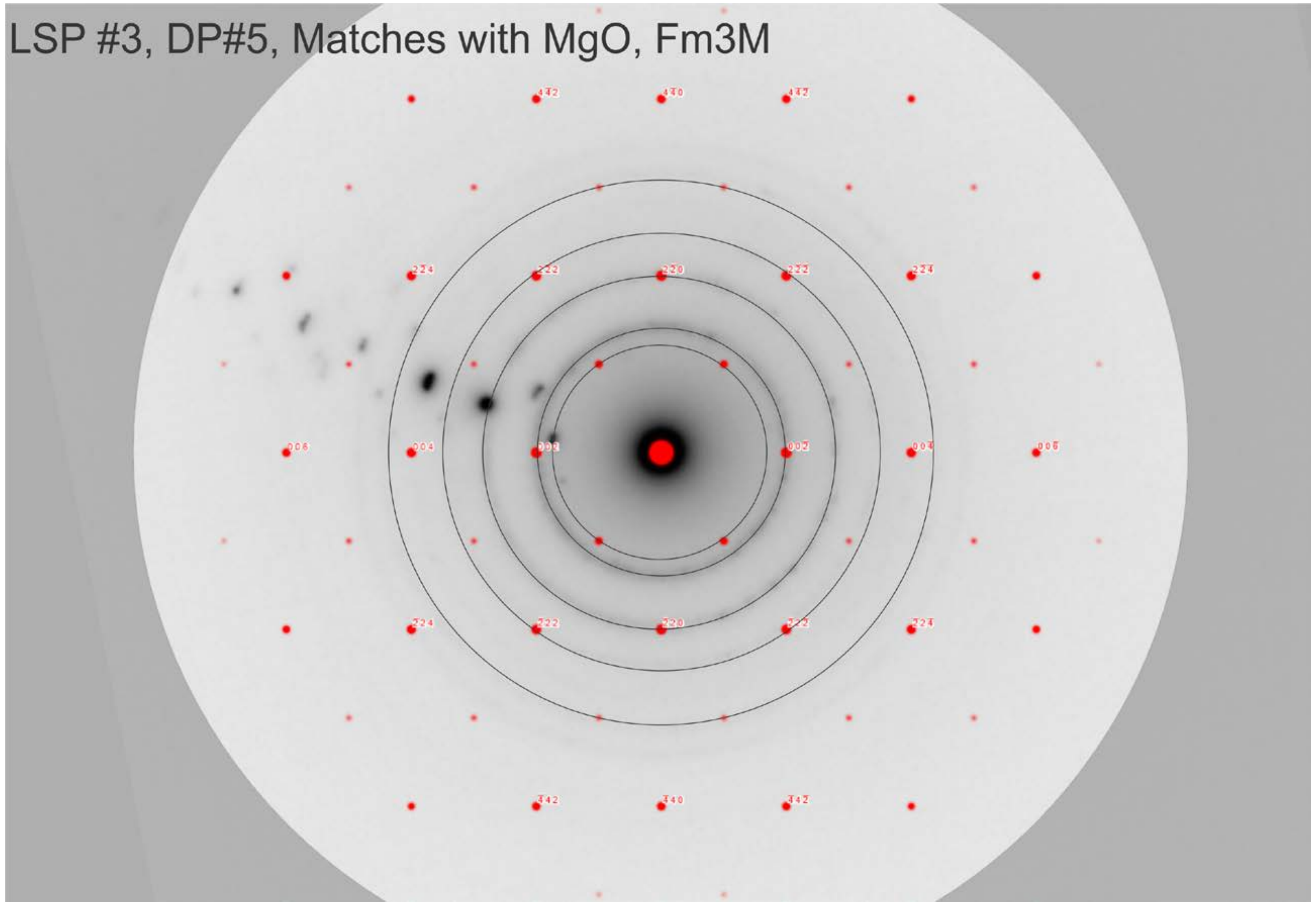
# Structural information of the LSP surface film using Selected Area Electron Diffraction (SAED) pattern




- Multiple diffraction patterns were obtained from the top surface film in LSP sample
- Typical ring patterns are noted, indicative of polycrystalline structure, with very fine grain size

# SAED Pattern of LSP Surface Film Appears to be Mg-oxide Type Phase




- LSP surface film seems to have structure similar to fcc MgO (Periclase) phase

Currently used TEM characterization techniques not able to provide structural information about the Al-rich phase